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Alkaline pretreatment and the synergic effect of water and tetralin enhances the liquefaction efficiency of bagasse

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HIGHLIGHTS

- Sugarcane bagasse was liquefied in a water/tetralin mixed solvent.
- The mixed solvent showed significantly synergic effect on bagasse liquefaction.
- The compositions of heavy oil obtained in different solvents are quite different.
- Alkaline pretreatment enhanced bagasse liquefaction in water-containing solution.

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ABSTRACT

Bagasse liquefaction (BL) in water, tetralin, and water/tetralin mixed solvents (WTMS) was investigated, and effects of tetralin content in WTMS, temperature, and alkaline pretreatment of bagasse on liquefaction efficiency were studied. At 300 °C, bagasse conversion in WTMS with tetralin content higher than 50 wt% was 86–87 wt%, whereas bagasse conversion in water or tetralin was 67 wt% or 84 wt%, respectively. Because the solid conversion from liquefaction in WTMS with tetralin content higher than 50 wt% was always higher than that in water or tetralin at temperatures between 250 and 300 °C, a synergic effect between water and tetralin is suggested. Alkaline pretreatment of bagasse resulted in significantly higher conversion and heavy oil yield from BL in water or WTMS. The effect of deoxygenation by the present liquefaction method is demonstrated by lower oxygen contents (16.01–19.59 wt%) and higher heating values (31.9–34.8 MJ/kg) in the produced oils.

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1. Introduction

Recently, biomass-derived liquid fuels, including bio-oil, bio-ethanol, and biodiesel, have attracted attention as potential renewable energy sources (Mazaheri et al., 2010; Yang et al., 2014). In the past decades, technologies using food crops such as corn and soybean to produce bio-ethanol and biodiesel have received considerable attention. However, fuel production from these food crops faces increasing competition with direct use of these crops as food and animal feed, which has an impact on both the availability and the price of these crops (Wu et al., 2011; Wang et al., 2011). Instead, thermochemical processes such as pyrolysis, gasification, and direct liquefaction allow the production of bio-oil from abundantly available and inexpensive non-food biomass materials such as agricultural residues and forestry wastes (Rezzoug and Capart, 2003; Yaman, 2004). While both pyrolysis and gasification require high operating temperatures, direct liquefaction requires less energy and can be consequently carried out at relatively low temperatures.

Usually, direct liquefaction is carried out under specific temperature and pressure conditions in the presence of solvents and/or catalysts. Since water is environmentally benign and inexpensive, it is one of the most studied solvents, mainly used as supercritical water. However, due to harsh operating conditions such as high temperature and pressure, most studies on this process have been carried out as lab- or bench-scale experiments (Toor et al., 2011; Qian et al., 2007). Several recent studies reported that liquefaction

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Abbreviations: BL, bagasse liquefaction; DTG, differential thermogravimetric; E_a, activation energy; HHV, high heating value; HO, heavy oil; SR, solid residue; Tb, burnout temperature; TG, thermogravimetric; TL, tetralin liquefaction; Tp, temperature corresponding to the peak height; WL, water liquefaction; WTMS, water/tetralin mixed solvents.

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of pinewood in the presence of various organic solvents, such as acetone and ethanol, improved the bio-oil yield and solid conversion (Liu and Zhang, 2008; Wang et al., 2013). However, due to their high volatility, utilization of these low molecular weight solvents likely increases the reaction pressure. In contrast, tetralin, a hydrogen donor solvent with high boiling point (207 °C), has been widely used as a solvent for coal liquefaction. Interestingly, liquefaction of pure cellulose by using tetralin resulted in a high solid conversion of 90 wt% (Demirbas, 2000). It is suggested that tetralin is able to dissolve, disperse, and stabilize the free radicals produced in the liquefaction process while preventing the repolymerization of intermediate products (Ogi and Yokoyama, 1993). Recently, biomass liquefaction in mixed solvents, especially organic solvent-water mixtures, has received much attention (Cheng et al., 2010; Chen et al., 2014; Zhao et al., 2013). These studies demonstrated that methanol/water mixed solvents were better than a single solvent in enhancing the total bio-oil yield and conversion of woody biomass (Zhao et al., 2013; Cheng et al., 2010). However, to the best of our knowledge, biomass liquefaction in a water/tetralin mixed solvent (WTMS) has not been reported. Since water and tetralin are insoluble, the interplay between them is rather physical than chemical. WTMS as a solvent has the potential to combine the excellent decomposing ability of subcritical water with the ability of tetralin to act as a hydrogen donor solvent; this improves the liquefaction efficiency to its maximum.

In addition, pretreatment of biomaterials plays an essential role in increasing the yield of liquid products and improving the operational conditions of biomass liquefaction. Chen et al. (2014) reported that compared to untreated samples, physical pretreatment, including centrifugation and ultrasonication, of wastewater algae decreased the activation energy (E_a) of the thermal decomposition from 50.2 kJ/mol to 35.9 kJ/mol while increasing the biocrude oil yield from 30 wt% to 55 wt%. The studies of Liu et al. (2011) on the behavior of acid–chlorite pretreatment and hydrothermal liquefaction of cornstalk, indicate that acid–chlorite pretreatment, especially in hot-compressed water liquefaction at 200–240 °C increased the water-soluble bio-oil yield. Later, Liu et al. (2014) demonstrated that compared to untreated cypress liquefaction, alkaline pretreatment prior to hydrothermal liquefaction markedly increased the bio-oil yield from 27.5 wt% to 48.4 wt% at 300 °C, while suppressing repolymerization reactions and the formation of solid residues. However, as far as we know, only few attempts were made using alkaline pretreatment methods for biomass liquefaction using tetralin or WTMS as the liquefaction medium.

In the present study, sugarcane bagasse was used as a biomass sample. To understand the synergic effect of water and tetralin on biomass liquefaction, bagasse liquefaction (BL) was carried out in subcritical water, tetralin, and WTMS. Moreover, the influence of alkaline pretreatment on liquefaction efficiency and product distribution was investigated. Our results might help in understanding the mechanism of biomass liquefaction in mixed solvents, while being useful to develop efficient biomass utilization processes.

2. Methods

2.1. Materials

Sugarcane bagasse was obtained from Pumiao Paper Factory in the city of Nanning, located in southern China. After sugar production, it was piled for one more year after which the air-dried bagasse was crushed and screened. The fraction with particle size between 20 and 80 mesh was collected and used in all the experiments. The ground bagasse was dried at 110 °C for 24 h and kept in desiccators at room temperature. All chemicals were analytical reagent grade and used as received. The chemical composition was determined according to the corresponding Chinese Standards as follows: lignin, GB/T 2677.8-1994; holocellulose, GB/T 2677.10-1995; extractives, GB2677.6-1994; ash, GB/T 2677.3-1993. Cellulose content was determined by the nitric acid–ethanol method (Wang and Cheng, 2011). The content of hemicellulose was calculated by the difference between holocellulose and cellulose contents. All data were based on dry raw material. The elemental analysis of bagasse was conducted with a CHNS/O analyzer (CHNS 932). The results show that bagasse contains 48.63 wt% cellulose, 32.20 wt% hemicellulose, 19.51 wt% lignin, 2.40 wt% extractives, and 0.90 wt% ash. The content of carbon, hydrogen, oxygen, nitrogen, and sulfur in bagasse are 47.58 wt%, 6.29 wt%, 46.03 wt%, 0.08 wt%, and 0.02 wt%, respectively.

2.2. Alkaline pretreatment

Alkaline pretreatment of bagasse was performed as follows: 30 g of bagasse (20–80 mesh, dry basis), 0.03–3.6 g of NaOH (the dosage was 0.1–12 wt% of bagasse), and 120 g of distilled water were weighed. NaOH was dissolved in the preweighed water, and the preweighed bagasse and NaOH solution were mixed in a polythene bag. The bag was sealed and kept for 23 h at room temperature. After that, the treated bagasse and the NaOH solution were used together in the subsequent liquefaction reaction.

2.3. Liquefaction procedure and product separation

All the liquefaction experiments were conducted in a 1000-ml stainless steel autoclave, with a magnetic stirrer (CFR-1, Yantai Jianbang Chemical Mechanical Co., Ltd., Yantai, China). The bagasse/solvent mass ratio was maintained at 1:8. In a typical liquefaction reaction, 30 g of bagasse and 240 g of solvent (water, tetralin, or a WTMS) were loaded in the autoclave. To liquefy NaOH-pretreated bagasse with water or WTMS as the solvent, 30 g of pretreated bagasse in wet state was loaded in the autoclave together with the alkaline solution and 120 g of solvent (water or tetralin). To liquefy NaOH-pretreated bagasse with pure tetralin as the solvent, the water content of 30 g of pretreated bagasse was removed by drying at 105 °C, after which it was loaded in the autoclave together with 240 g of tetralin.

After the reactants were mixed well, the reactor was sealed and purged three times with hydrogen to remove the air/oxygen in the reactor airspace. Agitation was set at 300 rpm and maintained for the duration of the experiment. The reactor was heated to the desired temperature (200–320 °C) at a rate of 5 °C/min by an external electric furnace and held for 60 min. It was then cooled to room temperature in a water bath. Once the reactor was cooled to room temperature, the reactor pressure was noted by a pressure gauge installed on the reactor head, and the gas produced was vented without being analyzed further. The liquid and solid products were collected from the bottom of the reactor. The mixture was filtered under reduced pressure through a preweighed filter paper to separate the insoluble material. The insoluble material and the reactor were further washed with dichloromethane and acetone successively until the washing solution became colorless. The collected washing solution was heated to 30 °C in a rotary evaporator to evaporate dichloromethane and acetone and then heated to 70 °C to evaporate water and residual solvents. After removal of the solvents, the obtained fraction was weighed and designated as heavy oil (HO). The insoluble material was rinsed with water and dried at 110 °C for 24 h; it was weighed and designated as solid residue (SR).

In addition, to study the effect of the solvent ratio on BL, the experiments were carried out with 30 g of untreated bagasse at 300 °C for 60 min. The bagasse/WTMS mass ratio was maintained at 1:8. The mass ratio of water/tetralin in WTMS was set at 1:0, 9:1, 1:1, 1:9, 1:14, and 0:1. The liquefaction procedure was the same as that described above.

The results obtained in this study are reported using the parameters defined as:

$$\text{Conversion (wt\%)} = (1 - W_{SR}/W_0) \times 100 \quad (1)$$

$$\text{HO yield (wt\%)} = W_{HO}/W_0 \times 100 \quad (2)$$

where W_0 is the weight of starting bagasse (dry, g), W_{SR} is the weight of solid residue (dry, g), and W_{HO} is the weight of heavy oil (dry, g).

2.4. Characterization

Thermogravimetric/differential thermogravimetric (TG/DTG) analysis of untreated bagasse and bagasse SR is useful to understand the liquefaction behavior of biomass. TG/DTG analysis was performed using a Q50 thermogravimetric analyzer (TA Instruments). All the samples were pre-dried in an oven at 105 °C for 24 h. During the TG experiment, about 9.5 mg of dried sample was placed in an alumina crucible and heated from 30 to 850 °C at a heating rate of 10 °C/min by using helium as a carrier gas at a constant flow rate of 100 ml/min.

HO samples were also analyzed using a gas chromatograph (GC17A, Shimadzu) coupled to a mass spectrometer (MS-QP5000, Shimadzu). The gas chromatograph was equipped with an auto sampler (AOC 20S, Shimadzu) and an Agilent HP-5MS column (30 m × 0.25 mm × 0.25 μm). Helium gas was used as the carrier gas at a fixed flow rate of 1.2 ml/min. The injected sample amount was 2 μl at a split ratio of 10:1. The column oven temperature was set at 60 °C for 5 min and then programmed with a heating rate of 10 °C/min until it reached 300 °C, which was held for 25 min. The injector and interface temperature were maintained at 290 °C and 310 °C, respectively. Mass spectrometry was performed with a scan range of 38–450 m/z and a scan frequency of 20 scan/s. The identification of components was performed by a similarity search on the NIST 1998 Mass Spectral database.

The elemental analysis of bagasse and HO was conducted with a CHNS/O analyzer (CHNS 932). The high heating value (HHV) of the sample was computed based on the Dulong formula (Xu and Lad, 2008).

$$\text{HHV (MJ/kg)} = 0.3383 * \text{C} + 1.422 * (\text{H} - \text{O}/8) \quad (3)$$

where C, H, and O represent the weight percentages of carbon, hydrogen, and oxygen, respectively.

3. Results and discussion

3.1. Effect of solvent ratio

Fig. 1 shows the effect of tetralin content in WTMS on the conversion and HO yield of bagasse liquefied at 300 °C for 60 min with a bagasse/WTMS mass ratio of 1:8. At tetralin amounts higher than 50 wt% of the total WTMS solvent, bagasse conversion was almost 20 wt% higher than BL in water, and was only slightly higher than BL in pure tetralin. The highest conversion and HO yield were obtained with WTMS in a water/tetralin mass ratio of 1:1 as solvent. These results indicate a synergic effect between water and tetralin in WTMS during BL.

Subcritical water has a low dielectric constant; it has weaker hydrogen bonds and a higher isothermal compressibility than ambient liquid water. It has the ability to break the rigid structure of lignocelluloses and consequently, decompose the lignocellulosic materials into smaller components by hydrolysis and subsequent reactions (Brunner, 2009). The presence of tetralin in WTMS favors the molecular rearrangement and stabilization of free radicals produced by pyrolysis and hydrolysis of biomass through hydrogen donors (Ogi and Yokoyama, 1993). In the present study, WTMS liquefaction is suggested to combine two advantages: the high decomposition ability of subcritical water and the excellent dissolving and hydrogen-supplying ability of tetralin. Therefore, it is suggested that the addition of tetralin to water facilitated the higher bagasse conversion into liquid and gas products.

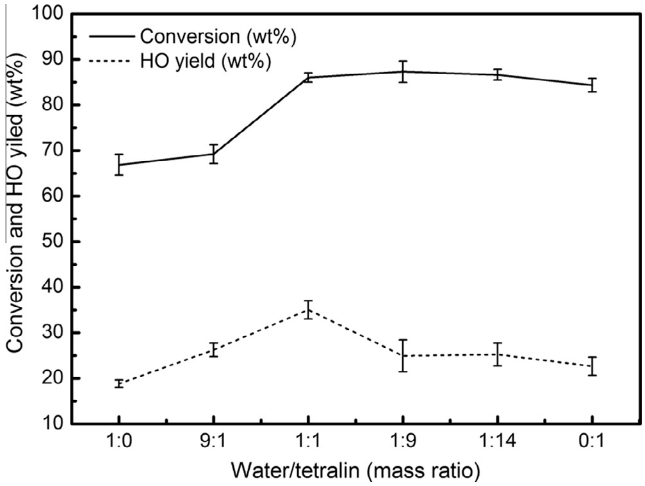

Fig. 1. Effect of tetralin content in WTMS on conversion and HO yield.

The thermal degradation properties of bagasse SR were analyzed by TG to understand the liquefaction behavior of bagasse in WTMS. The TG and DTG curves of bagasse SR from water liquefaction (WL), tetralin liquefaction (TL), and WTMS liquefaction (in a water/tetralin mass ratio of 1:1) at 300 °C are shown in Fig. 2. As a reference, the untreated bagasse was also analyzed and shown in Fig. 2. From the figure, it is clear that thermal degradation of the untreated bagasse takes place through a three-step process. Significant decomposition takes place at temperatures between 250 °C and 350 °C, which is followed by a gradual loss in mass at temperatures above 350 °C. Between 250 °C and 350 °C, the loss in mass is mainly due to the decomposition of hemicelluloses and cellulose, whereas the flat tailing section at higher temperatures is due to the decomposition of lignin (Mazaheri et al., 2013). Likewise, as the temperature increases from 220 °C to 520 °C, three peaks are observed in the DTG curve of the untreated bagasse. The peaks at around 220 °C and 320 °C represent the hemicellulose and cellulose decomposition peaks, respectively, whereas the third peak shows a wide temperature range from 370 °C to 520 °C, reflecting the decomposition of lignin (Chen and Kuo, 2010). Compared to the DTG curve of the untreated bagasse, DTG curves of bagasse SR showed one gentle peak between 270 °C and 400 °C and a bigger peak after 400 °C. These decomposition peaks are attributed to a relatively small amount of cellulose compounds and lignin, which have a particularly higher thermal stability. In other words, all the extractives, hemicelluloses, and a major part of the cellulose in the untreated bagasse decomposed during WL, TL, and WTMS liquefaction at 300 °C. In addition, similar to that observed in the untreated bagasse, a temperature corresponding to the peak height (T_p) of 485 °C and a burnout temperature (T_b) of 520 °C could be observed in the DTG curve of SR from TL. This indicates that most of the lignin remained in SR, which was not decomposed by TL. In contrast, although bagasse SR obtained from WL and WTMS liquefaction showed similar DTG curves, both showed higher T_p (525 °C) and T_b (575 °C) values, indicating that more lignin had been decomposed while some macromolecules with higher thermal stability were formed during WL and WTMS liquefaction. These macromolecules were insoluble

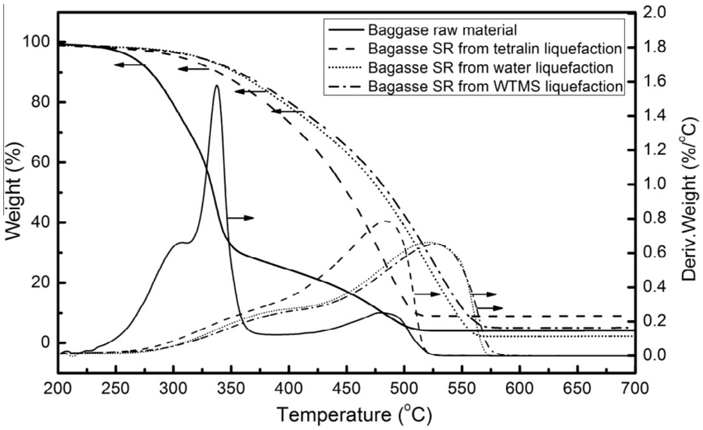

Fig. 2. TG/DTG curves of bagasse and solid residues from liquefaction in different solvents (water, tetralin, and WTMS).

in acetone and dichloromethane and existed as solid residues (Chen and Kuo, 2010). Obviously, as WTMS liquefaction resulted in a higher solid conversion, the yield of insoluble macromolecules formed from WTMS liquefaction was lower than that from WL.

The chemical composition of HO was identified by GC–MS, and the results are presented in Table 1. The components of HO are categorized into different groups according to the functional group and molecular structure (Fig. 3). The content of oxygenates and non-oxygenates in HO generated with different solvents are shown in Fig. 3a, whereas the components of HO categorized according to their functional groups are shown in Fig. 3b. Calculations were done using the peak area of the GC/MS chromatograms. As seen in Table 1 and Fig. 3a, HO derived from WL contained 88.4 wt% oxygenated compounds, similar to that obtained from WTMS liquefaction. When tetralin was used as the solvent, the fraction of oxygenated compounds was 51.5 wt%. The HO from WL contained 73.2 wt% phenolic compounds, 8.2 wt% ketones, and traces of esters and carboxylic acids. The HO from TL contained 41 wt% aromatic compounds, 14.9 wt% carboxylic acids, 13.7 wt% ketones, and 13.5 wt% phenols. Next to phenols as a main compound, WTMS (in a water/tetralin mass ratio of 1:1) greatly promoted the formation of ketones (27.8 wt%). In fact, light organic compounds such as ketones, organic acids, alcohols, and aldehydes are frequently soluble in water. Therefore, even though they were most likely produced through hydrolysis of hemicelluloses and cellulose, these oxygenated compounds were not identified in the HO derived from WL or WTMS liquefaction (Karagöz et al., 2004).

Previously, it was suggested that phenolic compounds in HO derive from the decomposition of lignin components (Cheng et al., 2010). Therefore, since large amounts of phenolic compounds were found in HO from WL, it is suggested that hot-compressed water contributes to the degradation of lignin. This is compatible with results from previous TG studies on bagasse SR showing that more lignin can be decomposed by WL and WTMS liquefaction. It has been suggested that biomass liquefaction in tetralin mainly follows solvolysis and thermal degradation reaction mechanisms (Beauchet et al., 2011). As such, aromatic compounds in HO from TL are likely to be formed by three mechanisms: (1) recombination and cyclization reactions via aldol condensation from C_2, C_3, and C_4 fragments, the initial degradation products of bagasse (Demirbas, 2000); (2) production of aromatic free radicals by bond cleavage of lignin at the liquefaction stage, which subsequently might attack other aromatic rings, resulting in the formation of higher molecular weight compounds through coupling reactions (Demirbas, 2000; Wang et al., 2007); (3) formation of naphthalene in HO, at least in part, via hydrogen release by tetralin (Beauchet et al., 2011).

Although the relative contents of phenolic and aromatic compounds in HO from WTMS liquefaction are intermediate to those of phenolic and aromatic compounds in HO from WL and TL, respectively, aldehydes, ketones, and esters, including 4-hydroxy-3,5-dimethoxybenzaldehyde, vanillin, 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone and 1-(4-hydroxy-3-methoxyphenyl)-ethanone, and 2,4-hexadienedioic acid, 3,4-diethyl-, dimethyl ester, are produced in higher amounts. As these aldehyde and ketone hydrocarbons have the 4-hydroxy-methoxyphenyl structure, they likely result from the cleavage of side aliphatic chain of the monomer lignin unit at α- or β-carbon atoms. These results indicate that some plant tissues in bagasse can only be decomposed by the mixed solvent, but not by water or tetralin.

In conclusion, as observed by Liu and Zhang, the three solvents were able to liquefy all hemicelluloses, a major part of cellulose, and a fraction of lignin in bagasse although lignin was resistant to solvolysis by tetralin (Liu and Zhang, 2008). Some insoluble macromolecules with high thermal stability were formed in WL and WTMS liquefaction. It is suggested that due to a synergic effect between water and tetralin, WTMS liquefaction yielded a higher conversion, resulting in the formation of ketones and aldehydes with a *p*-hydroxyphenyl structure.

3.2. Effect of temperature

Since the internal energy of macromolecules increases with temperature, resulting in the decomposition of macromolecules into lighter molecules (Zhuang et al., 2012), the operating temperature is one of the primary parameters for biomass liquefaction. BL was carried out in isometric WTMS (in a water/tetralin mass ratio of 1:1) at various temperatures ranging from 200 °C to 320 °C for 60 min, and compared with BL in water and pure tetralin. As seen in Fig. 4, the conversion of bagasse increased in a temperature-dependent fashion when water, tetralin, or WTMS was used as a solvent. Indeed, the conversion increased gradually in water, increased rapidly at a temperature between 270 °C and 280 °C in tetralin, and rose significantly at temperatures above 225 °C with WTMS as solvent. Moreover, at temperatures between 220 °C and 300 °C, conversion from BL in WTMS was always higher than that from BL in water or tetralin at the same temperature. It is assumed that different reaction mechanisms in different solvents might be responsible for this observation. Indeed, WL is achieved mainly by the hydrolysis reaction mechanism and TL mainly conforms to the solvolysis reaction mechanism (Beauchet et al., 2011), whereas WTMS liquefaction combines both hydrolysis and the solvolysis mechanisms through a synergic effect between water and tetralin. The synergic effect originated from not only their respective roles

Table 1
Compounds in HOs obtained from bagasse liquefaction in different solvents analyzed by GC–MS.

No.	RT (min)	Name of compound	Molecular formula	Solvent (area%)		
				Water	Tetralin	WTMS
1	9.26	Phenol	C_6H_6O	6.62	–	–
2	10.68	Naphthalene, decahydro-, trans-	$C_{10}H_{18}$	–	1.55	–
3	11.26	Phenol, 2-methyl-	C_7H_8O	1.86	–	–
4	11.46	Phenol, 2-methoxy-	$C_7H_8O_2$	10.22	–	2.92
5	11.59	Naphthalene, decahydro-, cis-	$C_{10}H_{18}$	–	5.12	–
6	11.80	Benzofuran, 2-methyl-	C_9H_8O	1.93	–	–
7	12.15	Bicyclo[4.3.0]nonane, 2-methylene-, (Z)-	$C_{10}H_{16}$	–	3.10	–
8	12.94	Phenol, 2-ethyl-	$C_8H_{10}O$	26.91	–	–
9	13.36	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	2.65	–	–
10	13.47	Naphthalene	$C_{10}H_8$	2.01	24.94	6.53
11	13.60	Benzofuran, 4,7-dimethyl-	$C_{10}H_{10}O$	0.96	–	–
12	14.82	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	9.19	2.58	–
13	14.88	1H-Inden-1-one, 2,3-dihydro-	C_9H_8O	1.77	–	–
14	15.28	1H-Inden-1-one, 2,3-dihydro-3,3-dimethyl-	$C_{11}H_{12}O$	1.42	–	–
15	15.97	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	14.12	3.58	10.27
16	16.11	Phenol, 2-methoxy-4-propyl-	$C_{10}H_{14}O_2$	1.59	–	–
17	16.38	1(2H)-Naphthalenone,3,4-dihydro-	$C_{10}H_{10}O$	–	1.61	–
18	16.39	Benzaldehyde, 4-hydroxy-	$C_7H_6O_2$	–	–	4.62
19	16.79	Vanillin	$C_8H_8O_3$	–	–	6.07
20	17.26	2,5-Dimethoxybenzyl alcohol	$C_9H_{12}O_3$	2.06	–	–
21	17.31	1,2,4-Trimethoxybenzene	$C_9H_{12}O_3$	–	2.49	–
22	17.33	Phenol, 4-methoxy-3-(methoxymethyl)-	$C_9H_{12}O_3$	–	–	2.60
23	17.51	Cetophenone, 4′-hydroxy-	$C_8H_8O_2$	–	–	3.86
24	17.98	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_9H_{10}O_3$	–	–	5.05
25	18.36	Benzene, 1,2,3-trimethoxy-5-methyl-	$C_{10}H_{14}O_3$	1.55	2.40	3.14
26	18.46	1H-Indene-1,5(6H)-dione, 2,3,7,7a-tetrahydro-7a	$C_{10}H_{12}O_2$	–	5.64	–
27	19.10	Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$	0.82	–	–
28	19.42	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (E,Z)-	$C_{12}H_{18}O_4$	3.52	3.20	–
29	20.17	Benzenepropanoic acid, 4-hydroxy-	$C_9H_{10}O_3$	–	12.26	–
30	20.19	2-Naphthalenol, 3-methoxy-	$C_{11}H_{10}O_2$	2.31	–	–
31	20.21	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	$C_9H_{10}O_4$	–	–	5.54
32	20.59	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	–	–	4.77
33	21.07	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	$C_{10}H_{12}O_4$	2.51	2.49	9.32
34	21.18	Beta.-(4-Hydroxy-3-methoxyphenyl)propionic acid	$C_{10}H_{12}O_4$	–	2.60	–
35	21.47	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (Z,Z)-	$C_{12}H_{18}O_4$	–	3.83	3.62
36	21.96	2H-1-Benzopyran-2-one, 3,5,7-trihydroxy-	$C_9H_6O_5$	2.48	–	2.50
37	22.44	2-(3-Isopropyl-4-methyl-pent-3-en-1-ynyl)-2-methyl-cyclobutanone	$C_{14}H_{20}O$	–	–	4.32
38	23.12	Phenol, 4-(1-methylpropyl)-	$C_{10}H_{14}O$	–	–	3.80
39	23.27	Pentadecanoic acid	$C_{15}H_{30}O_2$	1.43	–	–
40	24.47	Phenol, 4,4′-methylenebis-	$C_{13}H_{12}O_2$	–	–	3.05
41	25.33	Spiro[2.3]hexan-4-one, 5,5-diethyl-6-phenyl-	$C_{16}H_{20}O$	–	–	2.73
42	26.40	4,5-Diphenylocta-1,7-diene(meso)	$C_{20}H_{22}$	–	1.81	–
43	26.64	4,5-Diphenylocta-1,7-diene(dl)	$C_{20}H_{22}$	–	2.41	–
44	27.06	Methandrostenolone	$C_{20}H_{28}O_2$	–	2.42	–
45	27.10	4-Oxatricyclo[3.3.0.0(2,8)]oct-6-ene, 3-acetyl-3-methyl-	$C_{10}H_{12}O_2$	–	–	3.25
46	27.20	3,3-Dimethoxy-6,6-dimethyl-cyclohexa-1,4-diene	$C_{10}H_{16}O_2$	2.08	1.85	–
47	27.22	Homovanillyl alcohol	$C_9H_{12}O_3$	–	–	3.08
48	27.37	Benzene, (1,2-dicyclopropyl-2-phenylethyl)-	$C_{20}H_{22}$	–	2.85	–
49	27.53	2-Phenylpent-4-enol	$C_{11}H_{14}O$	–	3.93	–
50	27.65	Phenol, 2,6-dimethyl-4-nitro-	$C_8H_9NO_3$	–	2.22	–
51	29.20	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (E,Z)-	$C_{12}H_{18}O_4$	–	–	5.03
52	30.61	Phenol, 4,4′-methylenebis,2,6-dimethoxy-	$C_{17}H_{20}O_6$	–	5.12	–
53	31.33	2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester, (Z,E)-	$C_{12}H_{18}O_4$	–	–	–

–, Not detected.

of water and tetralin as solvents but also the interaction between water and tetralin during the liquefaction process. The presence of water in WTMS enhanced the flowability and diffusibility of tetralin by providing a higher reaction pressure. As such, the role of tetralin as a hydrogen donor solvent, capable of decomposing biomass through the solvolysis reaction mechanism, was enhanced. In addition, the presence of tetralin in WTMS prevented the repolymerization of intermediate products derived from the hydrolysis and solvolysis reactions, thereby decreasing the formation of solid residue.

Previously, Mazaheri et al. (2013) focused on the influence of an alkali catalyst on the liquid yield of oil palm shells via subcritical water liquefaction. Their results indicated that liquefaction at 287 °C resulted in a conversion of 58.3 wt%, whereas addition of 10 wt% NaOH into subcritical water liquefaction resulted in a high conversion of 83.1 wt% at the same temperature. Similar, while in the present study BL in water at 280 °C resulted in a conversion of 65.9 wt%, using WTMS as a solvent for BL led to a higher conversion of 81.4 wt% at the same temperature. This result suggests that water/tetralin mixed solvents and the addition of 10 wt% NaOH as a catalyst into subcritical water have similar effects on liquefaction conversion.

The thermal degradation of bagasse SR from WL and TL at different temperatures is shown in Figs. 5 and 6, respectively. The untreated bagasse was also tested as a reference, and the results are depicted in these figures. As can been seen from Fig. 5, TG

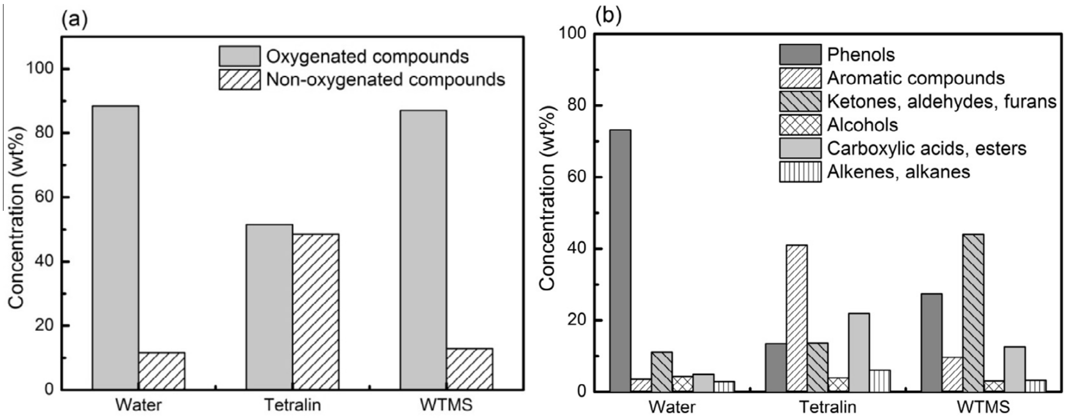

Fig. 3. Classification of the HO-composition obtained from BL at 300 °C for 1 h in three solvents. (a) Oxygenated compounds and non-oxygenated compound; (b) compounds categorized by functional groups and compound structure.

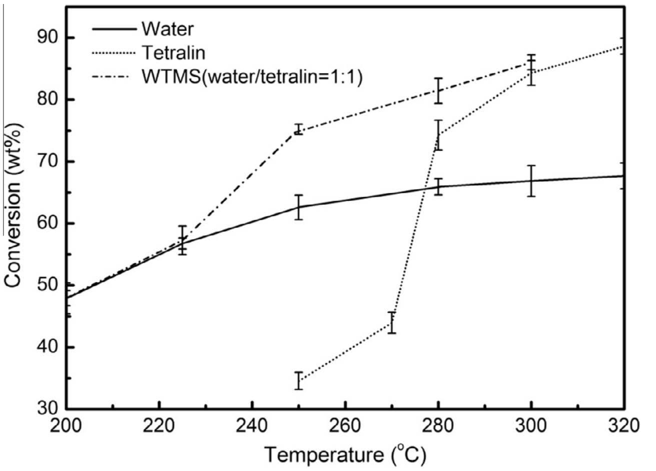

Fig. 4. Temperature effect on the conversion of bagasse liquefied in water, tetralin, and WTMS.

and DTG curves of bagasse SR from WL at different temperatures are very similar, except that SR obtained at 250 °C showed a higher loss in mass. The TG and DTG curves indicate that the decomposition of bagasse SR takes place in two stages. In the first stage, the weight decreased due to the decomposition of cellulose at temperatures between 260 °C and 400 °C. At the second stage, a significant loss in mass occurred due to the decomposition of lignin at temperatures ranging from 400 °C to 570 °C, when the rate of lignin decomposition became faster than that of cellulose degradation. From Fig. 5, it is clear that the extractive compounds, the hemicelluloses, and a major part of the cellulose in the untreated bagasse decomposed during WL. The decomposition of untreated bagasse completed at 520 °C, whereas the decomposition of three SRs obtained from WL at different temperatures completed at approximately 570 °C, indicating that some macromolecules having higher thermal stability were formed as solid residue during the WL process.

As shown in Fig. 6, DTG curves of bagasse SR from TL at 250 °C, 270 °C, and 280 °C show two peaks, whereas the DTG curve of bagasse SR from TL at 300 °C shows only one peak. These results indicate that many cellulose compounds still exist in SR obtained from TL at 250 °C and 270 °C, whereas almost all the cellulose compounds in bagasse were decomposed by TL at 300 °C. Additionally, similar to that observed with the untreated bagasse, the decomposition of all bagasse SR obtained at different temperatures was almost completed at approximately 525 °C. This suggests that the significant loss in mass, occurring between 350 °C and 525 °C, is due to the decomposition of lignin, whereas only a few insoluble solid residue macromolecules are formed in the TL process at temperatures between 250 °C to 300 °C. In other words, using tetralin as the solvent prevented the repolymerization of intermediate

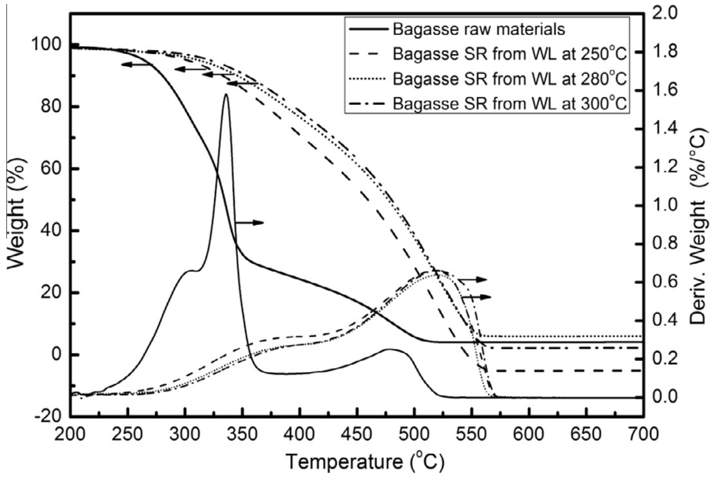

Fig. 5. TG/DTG curves of bagasse and solid residue from BL in water at different temperatures.

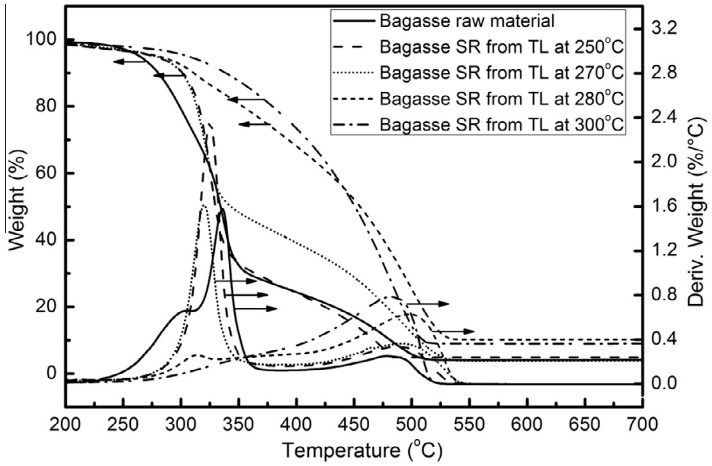

Fig. 6. TG/DTG curves of bagasse and solid residue from BL in tetralin at different temperatures.

Table 2
Effects of NaOH pretreatment on conversion and HO yield from BL in different solvents.

Amount of NaOH (wt%)	Conversion (wt%)			HO yield (wt%)		
	Water	Tetralin	WTMS	Water	Tetralin	WTMS
0.0	66.7	84.3	86.0	18.8	22.7	35.0
0.1	70.4	–	91.0	20.0	–	40.8
1.0	82.9	82.0	97.6	30.0	17.3	46.5
4.0	98.9	77.2	98.8	45.0	9.5	36.3

products, which, in turn, decreased the formation of solid residue macromolecules with high thermal stability.

From the above analysis, it is clear that the temperature conditions required by WL and TL to convert bagasse to liquid and gas products are greatly different. In WL, the decomposition of biomass, especially cellulose compounds, is a gradual temperature-dependent reaction. When tetralin is used as solvent, temperatures above 280 °C are required. As indicated in Figs. 2 and 4, WTMS liquefaction might remedy the defect of liquefaction by using pure water or pure tetralin as the solvent. In fact, WTMS liquefaction promoted the liquefaction efficiency by the synergic action between water and tetralin. The authors suggest that, even at lower temperatures, the higher reaction pressure in the WTMS liquefaction process caused by water (4.09 MPa at 250 °C compared to 0.29 MPa for TL at 250 °C) might have assisted tetralin in its role as a hydrogen donor solvent.

3.3. Effect of alkaline pretreatment

After alkaline pretreatment with 1.0 wt% NaOH followed by subsequent rinsing and drying, the bagasse contained 50.32 wt% cellulose, 27.58 wt% hemicelluloses, 19.58 wt% lignin, 1.98 wt% extractives, and 1.0 wt% ash. Compared to the composition of untreated bagasse, the hemicellulose content in the pretreated bagasse decreased by 4.62 wt%, whereas cellulose content increased only slightly and lignin content showed no obvious change. Table 2 shows the effect of NaOH pretreatment of bagasse on conversion and HO yield from BL at 300 °C for 1 h in the presence of water, tetralin, or WTMS (in a water/tetralin mass ratio of 1:1). Table 2 shows that: (1) regardless of NaOH pretreatment, the conversion and HO yield from BL in WTMS were higher than those from water or pure tetralin, demonstrating the synergic effect between water and tetralin in WTMS; (2) with increasing amounts of NaOH from 0.1 wt% to 4.0 wt%, the conversion and HO yield increased for BL in water and WTMS but decreased for BL in tetralin, indicating that NaOH pretreatment is only effective in enhancing the liquefaction efficiency of bagasse in water-containing solvents (water and WTMS), but has little effect on BL in tetralin; (3) pretreatment of bagasse with 4.0 wt% NaOH followed by WL, or pretreatment with 1.0 wt% NaOH, followed by WTMS liquefaction, both result in near complete conversions of bagasse of 98.9 wt% and 97.6 wt%, respectively. This suggests that NaOH pretreatment prevents repolymerization reactions of intermediate products and the formation of solid residues (Liu et al., 2014).

Earlier studies by Mazaheri et al. (2013), investigating the influence of an alkali catalyst on the yield of liquid products of oil palm shells by subcritical water liquefaction showed that the addition of 10 wt% NaOH in subcritical water liquefaction results in a high solid conversion of 84 wt%, 53.4 wt% yield of liquid products, and a low yield of gas products. It was assumed that the addition of NaOH accelerated the collapse of intramolecular and intermolecular hydrogen bonds in the oil palm shell structure and catalyzed the reduction and cracking reactions of macromolecules (Minowa et al., 1998). In the present study, the pretreatment of bagasse with NaOH ranging between 1.0 wt% and 4.0 wt% resulted in high conversions of 98.9 wt% and 97.6 wt% from WL and WTMS liquefaction, respectively. It is suggested that these high yields are due to changes in the composition and structure of bagasse caused by the alkaline pretreatment. According to our analysis, hemicelluloses in bagasse were partly dissolved during NaOH pretreatment. This result indicates that alkali pretreatment triggers the swelling of bagasse, which resulted in an increased internal surface area and a wider separation of structural linkages between holocellulose and lignin. As such, favorable conditions for the subsequent liquefaction reaction are created (Cağlar and Demirbas, 2001). Meanwhile, NaOH also acts as an alkali catalyst in the subsequent liquefaction process.

Even though NaOH pretreatment has little effect on TL of bagasse, the presence of tetralin in WTMS accelerated the conversion of solid bagasse to liquid products after NaOH pretreatment. These observations are likely explained by the following reasons: NaOH pretreatment significantly accelerated the action of water in the decomposition of biomass substrates through the hydrolysis reaction mechanism, while the synergic action between water and tetralin in WTMS promoted the solid conversion of bagasse to its maximum.

Table 3
Compounds in HOs obtained from liquefaction of NaOH-pretreated bagasse in different solvents analyzed by GC–MS.

No.	RT (min)	Name of compound	Molecular formula	Solvents		
				Water	Tetralin	WTMS
1	2.02	Acetic acid	$C_2H_4O_2$	–	7.58	–
2	3.29	Toluene	C_7H_8	–	1.03	–
3	3.37	Propane, 2,2-diethoxy-	$C_7H_{16}O_2$	2.43	31.47	12.92
4	5.09	Furfural	$C_5H_4O_2$	–	–	4.60
5	9.37	Phenol	C_6H_6O	5.10	–	0.89
6	10.58	Naphthalene, decahydro-, trans-	$C_{10}H_{18}$	–	–	1.95
7	11.40	Butanoic acid, 3-methylphenyl ester	$C_{11}H_{14}O_2$	–	1.91	–
8	11.45	Phenol, 2-methoxy-	$C_7H_8O_2$	10.50	–	–
9	11.49	Cyclohexanol, 5-methyl-2-(1-methylethyl)-	$C_{10}H_{20}O$	–	6.48	–
10	11.50	Naphthalene, decahydro-, cis-	$C_{10}H_{18}$	–	–	8.64
11	11.57	Furan, 2-butyltetrahydro-	$C_8H_{16}O$	–	1.73	–
12	12.05	Bicyclo[4.3.0]nonane, 3-methylene-	$C_{10}H_{16}$	–	1.72	3.21
13	12.97	Phenol, 4-ethyl-	$C_8H_{10}O$	28.33	–	–
14	13.22	Naphthalene	$C_{10}H_8$	5.76	17.26	26.62
15	13.43	1H-Indene-1,2-diol, 2,3-dihydro-	$C_9H_{10}O_2$	–	–	2.13
16	13.59	Phenol, 2,4,6-trimethyl-	$C_9H_{12}O$	–	–	5.56
17	13.75	Naphth[1,2-b]oxirene, 1a,2,3,7b-tetrahydro-	$C_{10}H_{10}O$	–	–	1.46
18	13.84	Hydroquinone	$C_6H_6O_2$	–	2.34	–
19	13.85	Benzene, cyclopentyl-	$C_{11}H_{14}$	–	–	2.23
20	14.00	3-Phenyl-3-pentene	$C_{11}H_{14}$	–	–	3.97
21	14.12	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	$C_{10}H_{16}$	–	–	2.00
22	14.26	Benzene, 2-ethenyl-1,3,5-trimethyl-	$C_{11}H_{14}$	–	–	3.55
23	14.48	Benzene, (3-methyl-2-butenyl)-	$C_{11}H_{14}$	–	–	2.59
24	14.64	1,2-Benzenediol, 3-methoxy-	$C_7H_8O_3$	–	–	–
25	14.77	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	8.89	1.40	3.92
26	14.91	3-Isopropylidene-5-methyl-hex-4-en-2-one	$C_{10}H_{16}O$	–	–	2.01
27	15.30	Naphthalene, 1-methyl-	$C_{11}H_{10}$	–	1.50	–
28	15.90	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	13.99	3.97	2.84
29	16.07	Spiro[4.5]dec-7-en-6-one, 7-hydroxy-	$C_{10}H_{14}O_2$	–	0.95	–
30	16.68	Naphthalene, 1,5-dimethyl-	$C_{12}H_{12}$	–	1.23	–
31	16.80	Vanillin	$C_8H_8O_3$	–	–	0.88
32	16.88	Naphthalene, 2,3-dimethyl-	$C_{12}H_{12}$	–	1.98	1.40
33	17.24	Phenol, 4-methoxy-3-(methoxymethyl)-	$C_9H_{12}O_3$	–	1.65	–
34	18.05	Furan, 2-(2-furanylmethyl)-5-methyl-	$C_{10}H_{10}O_2$	1.91	–	–
35	18.28	Benzene, 1,2,3-trimethoxy-5-methyl-	$C_{10}H_{14}O_3$	2.44	2.38	–
36	18.45	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{12}O_3$	–	1.32	–
37	19.01	Hexadecane	$C_{16}H_{34}$	1.83	1.39	1.50
38	19.35	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (E,Z)-	$C_{12}H_{18}O_4$	–	1.18	–
39	20.16	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	$C_9H_{10}O_4$	–	–	1.35
40	20.17	2-Pentanone, 3-(phenylmethylene)-	$C_{12}H_{14}O$	5.50	–	–
41	20.23	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$	–	–	0.94
42	20.50	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	2.11	–	–
43	20.98	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	$C_{10}H_{12}O_4$	3.25	0.85	1.36
44	21.37	2-Pentanone, 1-(2,4,6-trihydroxyphenyl)	$C_{11}H_{14}O_4$	–	2.68	–
45	21.39	Dodecane, 4,9-dipropyl-	$C_{18}H_{38}$	–	–	1.47
46	21.99	Spiro[5.6]dodecane-7,12-dione	$C_{12}H_{18}O_2$	2.36	–	–
47	22.35	Delta.-Selinene	$C_{15}H_{24}$	1.67	–	–
48	23.23	Eicosanoic acid	$C_{20}H_{40}O_2$	1.90	–	–
49	26.31	4,5-Diphenylocta-1,7-diene(meso)	$C_{20}H_{22}$	–	0.99	–
50	26.54	4,5-Diphenylocta-1,7-diene(dl)	$C_{20}H_{22}$	–	1.11	–
51	27.29	Benzene, (1,2-dicyclopropyl-2-phenylethyl)-	$C_{20}H_{22}$	–	1.28	–
52	29.90	7-(3,4-Methylenedioxy)-tetrahydrobenzofuranone	$C_{15}H_{12}O_5$	2.04	–	–

–, Not detected.

Table 3 shows the composition of HO derived from different solvents using NaOH-pretreated bagasse obtained with GC–MS analysis. The components of HO are categorized into different groups according to functional group and molecular structure and are shown in Table 4. As shown in Table 4, HO derived from WL, TL, and WTMS liquefaction contained 88.3 wt%, 65.5 wt%, and 38.5 wt% oxygenated compounds, respectively. Phenol and its derivatives are the main components in HO with water as the solvent (68.9 wt%), but decrease obviously to 7.0 wt% and 13.2 wt% in HOs with tetralin and WTMS as the solvent, respectively. Meanwhile, ketones, aldehydes, and aromatic compounds increased in HO with tetralin and WTMS as solvent. Compared with phenol contents in HO from liquefaction of the untreated bagasse (see Fig. 3b), phenol contents in HO from liquefaction of NaOH-pretreated

Table 4
Composition classification of HOs obtained from liquefaction of NaOH-pretreated bagasse at 300 °C for 1 h in three solvents.

Composition classification	Solvents		
	Water	Tetralin	WTMS
Oxygenated compounds	88.31	65.53	38.46
Non-oxygenated compounds	11.69	34.47	61.54
Phenols	68.92	7.02	13.21
Aromatic compounds	8.20	27.02	46.98
Ketones, aldehydes, furans	17.49	43.07	23.13
Alcohols	–	9.08	2.13
Organic acids, esters	1.90	9.49	–
Alkenes, alkanes	3.50	5.21	14.56

Table 5
Elemental analysis of HOs obtained from BL at 300 °C in different solvents using different bagasse samples: un-pretreated bagasse and NaOH-pretreated bagasse, which were compared with that of bagasse raw materials.

Solvent	Elemental composition (wt%)			HHV (MJ/kg)	O/C (molar ratio)	H/C (molar ratio)
	C	H	O			
Baggasse	47.58	6.29	46.03	16.86	0.73	1.59
Water[a]	65.43	7.28	27.24	27.65	0.31	1.34
Tetralin[a]	71.78	7.22	20.96	30.82	0.22	1.21
WTMS[a]	69.61	7.15	23.17	29.60	0.25	1.23
Water[b]	72.78	7.58	19.59	31.92	0.20	1.25
Tetralin[b]	74.23	8.50	17.22	34.14	0.17	1.37
WTMS[b]	75.41	8.54	16.01	34.81	0.16	1.36

[a] Unpretreated bagasse.
[b] NaOH-pretreated bagasse.

bagasse in three different solvents decreased to a varying degree, indicating that NaOH pretreatment suppressed the formation of phenols. The presence of more ketones and aldehydes in HO from WL of NaOH-pretreated bagasse might be a result of the ability of NaOH to stabilize the intermediate products obtained from the liquefaction reaction.

Table 5 shows the elemental components of the raw materials and HO products from BL in different solvents using NaOH pretreated and untreated bagasse. After bagasse is converted to HO products, significant reduction in oxygen content can be observed. Among the solvents, WTMS and tetralin are more effective in deoxygenation as the derived HO contains 16.01 wt% and 17.22 wt% of oxygen, respectively. Due to the lower O/C and higher H/C molar ratio, the HO generated with tetralin and WTMS are of better quality than those generated in water. The HHV of HO was 31.92–34.81 MJ/kg, higher than those using the untreated bagasse (27.65–30.82 MJ/kg) or those of lignin (23.3–26.6 MJ/kg) (Liu and Zhang, 2008). Taken together, pretreatment of bagasse with NaOH not only had a significant effect on the conversion and HO yield (as seen in Table 2), the quality of HO also improved as the oxygen content decreased whereas the hydrogen content and the HHV increased. As such, by including NaOH pretreatment of the materials, the current results reveal a new pathway to convert bagasse to liquid products via WL or WTMS liquefaction.

4. Conclusions

Decomposition of bagasse in water, tetralin, and WTMS was investigated using a batch-type reactor. The effects of tetralin content in WTMS, temperature, and alkaline pretreatment of bagasse on liquefaction efficiency were studied. The conversion and HO yield from BL at 300 °C in WTMS (water/tetralin mass ratio of 1:1) were significantly higher than those from BL in water or tetralin. This result indicates a synergic effect between water and tetralin, mainly originating from their respective roles as solvents and the interaction between water and tetralin during liquefaction process. NaOH pretreatment significantly enhanced liquefaction efficiency of BL in water or WTMS.

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